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## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Improvements in or relating to Bleaching Cellulose Pulp

We, MO OCH DOMSJO ARTIEBOLAG, a Swedish body corporate, of Ornskoldsvik, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

THIS INVENTION concerns bleaching cellulose pulp and, more particularly, concerns a method of increasing the resistance to brightness reversion and degradation in the ageing of bleached cellulose pulp.

It is possible to bleach most cellulosic materials to a high degree of brightness by treatment with one or more of the following: chlorine, hypochlorites, chlorine dioxide, chlorites and peroxides in several steps including intermediate washing and alkali steps. In many cases, however, this brightness is not permanent and the decrease in brightness is often accompanied by a degradation of the carbohydrate material. These changes, which occur in the subsequent processing or use of the material, are slow, however, and depend on the environment, such as temperature, moisture, light and the presence of acidic or alkaline, oxidizing or reducing compounds. Hence, for technical investigations of the resistance to ageing of the finished cellulose pulp, it is in most cases necessary to resort to accelerated tests, such as the use of an elevated temperature, which makes it possible to obtain measurable changes in a short time.

Several different methods of rapidly ageing cellulosic materials are in use. Intense illumination is often employed in the dye industry but this usually yields results which are difficult to interpret when applied to cellulosic materials since the light appears to bleach the coloured reaction products to a varying degree. Frequently, heating at temperatures above 100°C. for from 2 to 24 hours is employed, a practical period being 16 hours (i.e. a one day pause in the working time) [Price 4s. 6d.]

at 120°C. This method involves heating the cellulosic material in an anhydrous condition, while in practical use and most frequently in processing it practically always contains some water, and it is probably more suitable generally to use a temperature below 100°C. and an atmosphere of high relative humidity. A practical procedure for the latter method is to heat for 16 hours at 80°C. in a closed vessel of about 80% relative humidity, obtained by means of a mixture of crystals and aqueous salt solution of the overall composition  $\text{Na}_2\text{CO}_3 + 10 \text{H}_2\text{O}$ .

The above two methods of accelerated ageing frequently give quite different gradings for sulphite and sulphate pulps treated in different ways. For example, the yellowing of sulphite and sulphate pulps may be different and depends on various factors, such as content of extract, carbonyl (high copper number), residual lignin, carboxyl, heavy metal salts and unremoved degradation products. In some cases, such as hardwood sulphate pulp, it can be shown that although the pulp has been bleached carefully in several steps, finally treated with the specific lignin removing agent chlorine dioxide, and the pulp has been rendered free from extract and, by reduction with borohydride, from carbonyl groups and has a low content of heavy metal salts, the yellowing is relatively high. It has been suggested that this is due to the fact that hemicellulose which is present in large proportions in e.g. birch sulphate pulp, is less resistant than cellulose.

We have now found that the resistance to brightness reversion and degradation in the ageing of bleached cellulose pulp can surprisingly be increased by treating said pulp for 1 to 6 hours with water or an aqueous solution of a mineral acid or an alkali, the concentration of which is such that the pH of the solution is between 2 and 12, at a temperature above 80°C., especially above 95°C., prior to or after bleaching or as an

intermediate step between any of the bleaching steps in the bleaching procedure.

Substantially better results are obtained if a major proportion of the lignin is removed prior to the treatment. It is found that the pH of the water also greatly influences the result of the treatment in that it appears to be less satisfactory around the neutral point. A strongly acid solution (pH 2.5 to 4.0) tends to cause degradation but it results in a satisfactory brightness stability in the ageing test at 80°C. and 80% relative humidity whilst a weakly alkaline solution (pH 10.0 to 11.5) results in a low rate of reaction, but little change of the strength properties of the pulp and results in a satisfactory brightness stability in the ageing test at 120°C. Additions of small amounts of certain substances, for example reducing agents as well as oxidizing agents, seem beneficially to influence the degradation or ageing resistance of the pulp. The aqueous solution of the acid or alkali therefore preferably contains a small amount of other substances to neutralise or destroy absorbed or bound chemicals remaining in the pulp from previous bleaching steps or treatments, whereby to obtain optimum pH and redox potential values for the pulp treatment. In addition it is preferred that a small amount of at least one substance which either increases the decomposition of impurities by the water or protects the carbohydrates from degradation, or both, is added. It will, of course, be readily apparent to those skilled in the art that the treatment of this invention should preferably be carried out on well washed pulp, so that it is as free from chlorine as possible to avoid degradation of the cellulose. Pulps containing chlorine can be treated in accordance with the invention to improve the resistance to brightness reversion, but the strength properties of such treated pulps are inferior to those of treated chlorine-free pulps.

It will be seen from the above that if a bleaching step precedes the treatment with water, additions may be necessitated to neu-

tralize the action of unremoved or slightly soluble substances carried over from said bleaching step. The position of the treatment with water in a bleaching schedule will therefore be determined largely on the basis of economic considerations.

The period of time for which the treatment is carried out depends, within the limits of 1 to 6 hours, of course, on the temperature used and the final result desired.

The invention is more particularly described in the following Examples, which are given by way of illustration. Example 1 shows the effect obtained in initial experiments and does not indicate how the greatest possible resistance can be obtained at the lowest cost or with minimum degradation. In the Examples brightness figures are given on the % SCAN scale. The SCAN method of determining brightness is described in English in Svensk Papperstidning 65 (1962), 545-548.

#### EXAMPLE 1

A cooked, washed and screened birch sulphate pulp was pre-bleached in the following manner:

1. Chlorination with 4.0% chlorine (all chemical changes based on the weight of the absolutely dry pulp) for 1 hour at 4% pulp consistency and a temperature of 20°C., followed by washing the chlorinated pulp first with water at 20°C. and then with water at 50°C., and draining the pulp.

2. An alkaline wash at 50°C. and 6% pulp consistency with 1.7% solution of sodium hydroxide for 2 hours, the pH being finally 11.0, followed by washing with water at 40 to 50°C.

3. Bleaching with 1.2% active chlorine as hypochlorite and 0.6% sodium hydroxide at 40°C. and 6% pulp consistency for 2 hours, the final residual chlorine content being 0.3% at a final pH of 11.6, followed by washing with water at 40 to 65°C.

4. Bleaching with chlorine dioxide (1.2% available chlorine) for 3 hours at 65°C. and 6% pulp consistency and a final pH of 3.6, followed by washing with water at 40 to

Poor quality

65°C.

The resulting pulp was divided into six batches each of which was treated as indicated below in Table I.

TABLE I

Batch	A	B	C	D	E	F
<u>Treatment</u>						
<u>Alkali</u>						
0.7% NaOH, pH	—	—	—	11.5	11.5	11.5
<u>Water treatment, °C</u>	—	—	120	100	120	120
2 hrs., pH	—	—	3.95	6.9	6.3	3.1
%SO <sub>2</sub>	0	0	0	0	0	0.4
<u>Alkali</u>						
0.7% NaOH, pH	11.3	11.3	11.4	—	—	—
<u>2nd ClO<sub>2</sub>, %</u>	0.5	0.7	0.7	0.7	0.7	0.7
<u>Temp. 70°C.,</u>						
Time, hours	4	6	3	3	3	3
pH	4.4	4.4	3.9	3.9	3.7	3.0
<u>Results</u>						
Brightness, air dry						
pulp, %SCAN	93.1	93.0	91.4	93.0	93.0	93.0
„ after ageing at 80°C. %SCAN	84.0	84.0	87.1	83.9	85.1	86.0
„ after ageing at 120°C. %SCAN	83.6	83.1	82.2	84.2	86.2	83.2
<u>Viscosity, cps.</u>	120	100	60	100	80	80
<u>Yield, %</u>	99	99.5	99	99.5	98	98.5

5 In the above table, batches A and B were not subjected to the treatment with water, but are included as controls. It will be seen that it is possible to obtain the beneficial effect either in the accelerated ageing test at 80°C., 80% relative air humidity or in the accelerated ageing test at 120°C. absolutely dry. The brightness of the air dry pulp is constant or somewhat reduced, but it is possible

to carry out the treatment so that this brightness is increased somewhat, although little compared to the brightness after ageing. The yields indicated, which are probably uncertain within about 1%, have been shown to demonstrate that the treatment does not cause an appreciable dissolution of hemicellulose or cellulose and thus does not suffer from the disadvantage of the hot alkali refinement

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which has been used in the manufacture of rayon pulp. The latter process also causes a marked viscosity reduction, normally at least to 50 cps. or below. In other experiments, it was established that the pentosan (i.e. hemicellulose) content is not reduced appreciably more than the experimental error inherent in the experiment, and that the carboxyl group content, which is also high for the pulp tyre investigated, is not reduced by more than about 10%.

The above series of experiments was the first one in which the effect of the treatment was demonstrated with certainty. The Examples 2 and 3 below show that considerably better effects are obtainable by a careful choice of temperature, time and pH conditions depending on the type of pulp treated.

#### EXAMPLE 2

A cooked, washed and screened birch sul-

phate pulp was pre-bleached as set out below:

1. Chlorination with 4.0% chlorine for 1 hour, at 4% pulp consistency and a temperature of 20°C., followed by washing the chlorinated pulp with water at 20°C. and then with water at 50°C. and draining the pulp.

2. Alkaline washing at 50°C. and 6% pulp consistency with 1.7% solution of sodium hydroxide for 2 hours, the final pH being 11.0, followed by washing with water at 40 to 50°C.

3. Bleaching with 1.2% active chlorine as hypochlorite and 0.6% sodium hydroxide at 40°C. and 6% pulp consistency for 2 hours, the final residual chlorine being 0.3% and pH 11.6, followed by washing with water at 40°C.

The pulp was divided into two batches of which one was finally bleached according to the schedule below while the other one was

treated with water as also set out below.

TABLE II

Batch	G	H
<u>Water Treatment</u>		
2 hours, 120°C.		
pH	—	11.0
% NaOH	—	1.5
<u>1st ClO<sub>2</sub></u>		
3 hours		
0.8% ClO <sub>2</sub> , 70°C.		
pH	3.85	4.20
<u>Alkali treatment</u>		
105 min.		
0.7% NaOH, 50°C.		
pH	11.50	11.65
<u>2nd ClO<sub>2</sub></u>		
3 hours		
0.6% ClO <sub>2</sub> , 70°C.		
pH	4.35	4.25
<u>Results</u>		
Brightness, air dry pulp, % SCAN	92.5	93.0
„ after ageing at 80°C., % SCAN	82.1	86.0
„ after ageing at 120°C., % SCAN	79.0	85.5
<u>Viscosity, cps.</u>	100	80
<u>Yield, %</u>	98.0	96.2

5 The Example shows that treatment at pH 11.0 and 120°C. after the pre-bleach step markedly improves the brightness of birch sulphate pulp after ageing at 80°C. as well as 120°C. without appreciable reduction in viscosity.

## EXAMPLE 3

A cooked, washed and screened pine sulphate pulp was pre-bleached as set out below:

1. Chlorination with 7.0% chlorine for 1 hour, at 4% pulp consistency and 20°C. temperature, followed by washing with water at

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20°C. and then with water at 45°C. and draining the pulp.

5 2. Alkaline washing at 45°C. and 6% pulp consistency with 2.2% sodium hydroxide for 1 hour, the final pH being 11.15, followed by washing with water at 40°C.

3. Bleaching with 1.9% active chlorine as hypochlorite and 0.8% sodium hydroxide at

40°C. and 6% pulp consistency for 2 hours, the final residual chlorine being 0.20% and final pH 11.0, followed by washing with water at 40°C.

The pulp was divided into three batches of which two batches were treated with water as shown.

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TABLE III

Batch	J	K	L
<u>Water treatment</u>			
2 hours, 100°C.			
pH	—	2.25	11.5
% SO <sub>2</sub>	—	0.5	—
<u>1st ClO<sub>2</sub></u>			
3 hours			
0.7% ClO <sub>2</sub> , 60°C.			
pH	2.80	2.60	3.10
<u>Alkali treatment</u>			
105 min.			
0.7% NaOH, 50°C.			
pH	11.55	11.55	11.55
<u>2nd ClO<sub>2</sub></u>			
3 hours			
0.6% of ClO <sub>2</sub> , 70°C.			
pH	3.85	3.90	4.00
<u>Results</u>			
Brightness, air dry pulp, % SCAN	93.4	93.1	93.8
„ after ageing at 80°C., % SCAN	82.9	86.4	87.1
„ after ageing at 120°C., % SCAN	84.3	85.2	88.7
<u>Viscosity, cps.</u>	54	49	50
<u>Yield %</u>	97.7	97.1	96.8

The results show that treatment both at pH 2.25 and at pH 11.5 and 100°C. after the pre-bleach step markedly improves the brightness of pine sulphate pulp when aged at both 80°C. and 120°C. without significant degradation of the cellulose.

The method of this invention has been found to be useful for softwood sulphate pulps as well as for hardwood sulphate pulps and can be applied to reduce the brightness reversion of sulphate pulps in general.

#### WHAT WE CLAIM IS:

1. A method of increasing the resistance to brightness reversion and degradation in the ageing of bleached cellulose pulp, which comprises treating said pulp for 1 to 6 hours with water or an aqueous solution of a mineral acid or an alkali, the concentration of which is such that the pH of the solution is between 2 and 12, at a temperature above 80°C. prior to or after bleaching or as an intermediate step between any of the bleaching steps in the bleaching procedure.
2. A method according to claim 1, in which the aqueous solution of the acid or alkali contains a small amount of other substances to neutralise or destroy absorbed or bound chemicals remaining in the pulps from previous bleaching steps or treatments, whereby to obtain optimum pH and redox potential values for the pulp in the treatment.
3. A method according to claim 1 or 2 in which a small amount of at least one substance which either increases the decomposition of impurities by the water or protects the carbohydrates from degradation, or both, is added.
4. A method according to any of claims 1 to 3 in which the treatment is carried out as an intermediate step in a bleaching process

using chlorite or chlorine dioxide as the bleaching agent.

5. A method according to any of the preceding claims in which the treatment is carried out at a temperature above 95°C.

6. A method according to any of the preceding claims in which a major proportion of lignin present is removed prior to the treatment.

7. A method according to any of the preceding claims, in which the pH of the solution is either 2.5 to 4.0 or 10.0 to 11.5.

8. A method according to any of the preceding claims in which the pulp is pre-bleached prior to the treatment.

9. A method according to any of claims 4 to 8 in which the cellulose pulp is cooked, washed, screened, chlorinated, washed with alkali and bleached with hypochlorite in a first step and washed, whereupon it is treated with water and finally bleached with chlorine dioxide in two steps with an intermediate alkaline treatment.

10. A method according to claim 1 of increasing the resistance to brightness reversion and degradation in the ageing of bleached cellulose pulp substantially as herein described.

11. A method according to claim 1 of increasing the resistance to brightness reversion and degradation in the ageing of bleached cellulose pulp substantially as described in any of the Examples.

12. Cellulose pulp which has been treated by a method as claimed in any of claims 1 to 11.

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## POOR QUALITY